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# Anhydrite-dissolution porosity in the Upper Muschelkalk carbonate aquifer, NE-Switzerland: implications for geothermal energy and geological storage of gas

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## Abstract

The Upper Muschelkalk carbonate aquifer within the Swiss Molasse Basin is currently being investigated for its potential for geothermal energy exploitation and geological storage of gas. Porosities of up to 25% are locally observed where early diagenetic (Triassic) anhydrite has been dissolved by groundwater. However, the dimensions and the spatial distribution of this type of cavernous porosity are not well known, as the Basin is underexplored. The present study reconstructs the genesis and evolution of these pores from drill-core studies, thus providing conceptual understanding to support ongoing exploration in the deeper, hotter southern regions of the Basin. The reconstruction is based on petrographic investigations, analyses of stable and radiogenic isotopes and fluid inclusion studies. The results show that the anhydrite dissolved during the Neogene upon influx of chemically modified meteoric runoff from uplifted crystalline domes in the Black Forest area of southern Germany. As this hydrogeological system is spatially restricted to the shallow, northern margin of the aquifer, we conclude that zones of anhydrite-dissolution porosity are unlikely to extend deeper into the Basin. Exploration in the deeper realms of the Basin should therefore target other types of porosity and permeability, e.g. sucrosic dolomite facies and fracture networks.

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## 1. Introduction

In the Swiss Molasse Basin (SMB), deep saline aquifers are one of the options under investigation for geothermal energy production and for storage of gas (seasonal methane and CO<sub>2</sub> sequestration). Particularly the Middle Triassic dolomites within the Upper Muschelkalk (Trigonodus Dolomit) show encouraging properties along the northern

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margin of the SMB<sup>1</sup>. Matrix porosity in the northern margin is locally high (<25%), in part due to the presence of vuggy beds that contain cm–dm scale cavities formed by dissolution of eogenetic anhydrite nodules. These pores are in some cases well connected, as reflected by permeabilities up to  $10^{-13}$  m<sup>2</sup>. A key question is whether dissolution-porosity can also be expected in the deeper, largely unexplored southern realm of the SMB, which is of more interest for geothermal and gas-storage applications. The present study reconstructs the genesis and evolution of the dissolution pores, thus providing conceptual understanding to support ongoing exploration. One hypothesis is that the dissolution is due to recent influx of meteoric water from the Black Forest Highlands situated north of the SMB (Fig. 1a). This hydrogeologic system developed in response to Neogene doming of the Black Forest area, which resulted in erosion of the Mesozoic sedimentary cover down to the crystalline basement and induced lateral infiltration of meteoric water towards the southeast<sup>2</sup> (Fig. 1b). Exfiltration occurs both towards the west (Rhein River system) and towards the northeast (Neckar River system)<sup>2</sup>. According to this hypothesis, dissolution porosity would be expected only along the northeastern margin of the SMB. A contrasting hypothesis is that the porosity is due to eo- or meso-genetic processes related to the Mid-Triassic depositional environment or its subsequent burial during the Mesozoic. In such a case, the high porosities could perhaps be expected throughout the SMB.

The reconstruction of the genesis and evolution of the anhydrite dissolution cavities is based on drill-core samples from two boreholes situated at Benken<sup>3</sup> (top Muschelkalk at 811 m depth) and at Schlattigen<sup>4</sup> (top Muschelkalk at 1112 m depth), and it includes standard petrographic investigations, analyses of stable and radiogenic isotopes (i.e.  $\delta D$ ,  $\delta^{18}O$ , and  $^{87}Sr/^{86}Sr$ ) of rock-forming (dolomite) and pore-filling (quartz, calcite and kaolinite) minerals and fluid inclusion studies of pore-filling quartz and calcite.

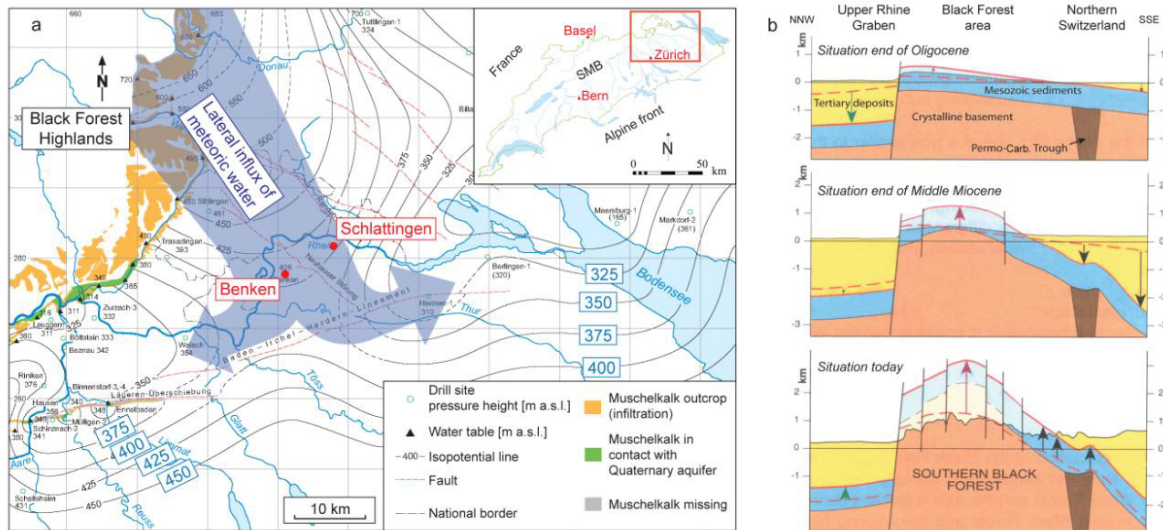


Fig. 1. (a) The recent hydrogeological system at Benken and Schlattigen (modified after Nagra<sup>2</sup>), which developed in response to (b) Oligocene–Neogene doming of the Black Forest<sup>5</sup> area. Inset in (a) shows location of Swiss Molasse Basin (SMB). The Upper Muschelkalk sits within the Mesozoic sediments marked blue in (b).

## 2. Results

### 2.1. Petrography

In some intervals of the Muschelkalk aquifer at Benken and Schlattigen the anhydrite dissolution cavities remain empty, but in others the pores have been affected by two events of mineral precipitation: (1) the first involved precipitation of quartz and minor pyrite and sphalerite, leading to only minimal clogging. The quartz crystals contain tiny inclusions of relict anhydrite, indicating that the quartz precipitated during anhydrite

dissolution; (2) a second event in which calcite and kaolinite precipitated, in part coevally, leading locally to complete clogging of pores.

## 2.2. Fluid inclusion studies

Primary fluid inclusions in pore-filling quartz contain methane–water mixtures, attesting to heterogeneous phase entrapment. Measurements of the homogenization temperatures of liquid-rich inclusions yield trapping temperatures in the range 41–52 °C (2 samples; 4 groups of coeval inclusions, i.e. “assemblages”) at Benken and 42–50 °C at Schlattingen (2 samples; 9 assemblages). The salinity of the trapped fluid is highly variable, ranging from 9 to 23 wt% NaCl<sub>eq</sub> at Benken and 5 to 23 wt% NaCl<sub>eq</sub> at Schlattingen. Salinity variations within individual assemblages are up to 17 wt% NaCl<sub>eq</sub>.

Heterogeneously trapped primary inclusions in pore-filling calcite at Schlattingen indicate trapping temperatures from 76 to 80 °C (4 samples; 4 assemblages). Homogeneously trapped primary inclusions at Benken yield only minimum trapping temperatures, between 76 and 85 °C (1 sample; 5 assemblages). The salinity of the trapped fluid ranges from low to intermediate values (0.7–3.2 wt% NaCl<sub>eq</sub> at Benken and 0.2–6.5 wt% NaCl<sub>eq</sub> at Schlattingen). Salinity variations within individual assemblages are commonly around 2.5 wt% NaCl<sub>eq</sub>.

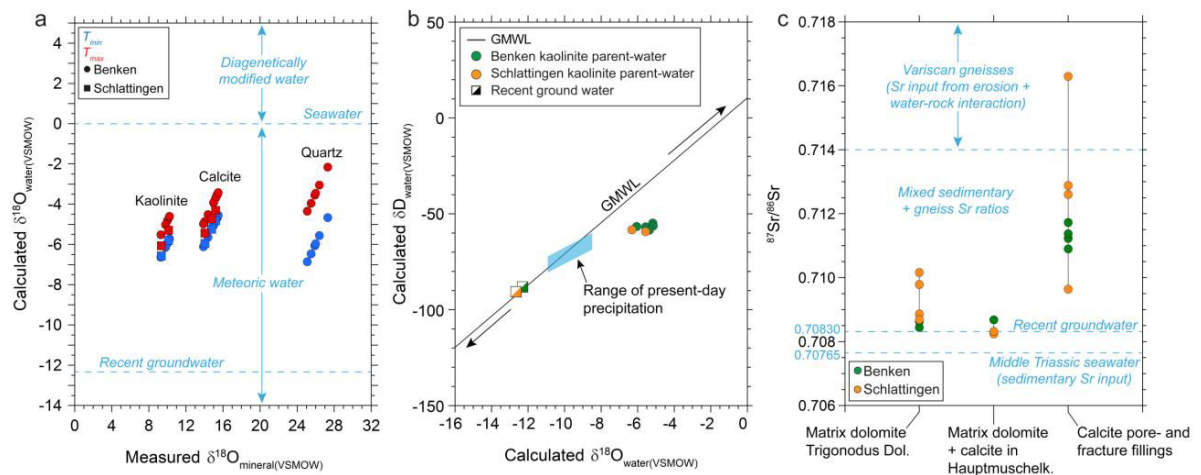


Fig. 2. (a) Calculated oxygen isotope composition of mineral parent-waters within the range of fluid inclusion trapping temperatures. (b) Calculated oxygen and hydrogen isotope composition of kaolinite (and calcite) parent water compared to the recent groundwater, the present-day precipitation and the Global Meteoric Water Line (GMWL). (c) Strontium isotope ratios for matrix samples of the Trigonodus Dolomit and the underlying Hauptmuschelkalk compared to those of calcite pore fillings.

## 2.3. Isotope analyses

The results of the stable and radiogenic isotope analyses of the various pore-filling minerals are given in Fig. 2. Stable isotope signatures of corresponding parent waters were calculated using the trapping temperatures of primary fluid inclusions and the fractionation factors of  $\alpha^6$  for the calcite–water system, of  $\alpha^7$  for the quartz–water system and of  $\alpha^8$  for the kaolinite–water system. The clear petrographic evidence that kaolinite and calcite partly co-precipitated is taken as evidence that the temperatures of mineral formation derived from the primary fluid inclusions in calcite are also valid for kaolinite.

## 3. Discussion

The highly variable salinity of fluid inclusions in quartz is interpreted to reflect mixing of two waters with contrasting salinities during anhydrite dissolution. The more saline endmember of this mixture, which was close to halite saturation, is likely to have been seawater modified by evaporation and diagenesis, that was originally trapped

within the rock pores during seepage-reflux dolomitization of the carbonate precursor of the Trigonodus Dolomit. The calculated  $\delta^{18}\text{O}$  signatures of the parent waters of pore-filling quartz and later calcite and kaolinite (Fig. 2a,b) reveal strong meteoric components. Thus, meteoric water constituted the lower salinity endmember of the mixture. Dilution of the original porewater in the Trigonodus Dolomit by influx of meteoric water was evidently responsible for dissolution of the anhydrite nodules and for the precipitation of calcite and kaolinite within the resulting dissolution cavities. The degree of dilution increased with time, as shown by the lower range in salinities of the parent-water of pore-filling calcite.

This mixing scenario is consistent with the highly elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the pore-filling calcite compared to the rock matrix (Fig. 2c). The only feasible sources of radiogenic Sr in the local stratigraphy are the Buntsandstein and the Variscan gneiss basement<sup>9</sup>, which have  $^{87}\text{Sr}/^{86}\text{Sr}$  values up to 0.7285. Although these units underlie the Muschelkalk at depth, they are separated by an intervening 10–20 m thick, low-permeability layer of evaporites (Anhydrite Group) that have non-radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  values. Consequently, infiltration of radiogenic porewater from the basement into the Muschelkalk through undisturbed sections of the Anhydrite Group is unlikely. On the other hand, the Buntsandstein and the Variscan gneisses are also exposed in the Black Forest Highlands to the north of the Muschelkalk (Fig. 1b). Meteoric water has interacted with these rocks since they were uplifted by Miocene block-faulting, and their salinity was presumably elevated early on by interaction with eroding Mesozoic evaporites. The increased salinity and prolonged water–rock interaction would have allowed these waters to acquire radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures. Topographically-induced southward flow of these chemically modified surface waters could have recharged the aquifer laterally (e.g. as is still happening today, Fig 1a). Alternatively, recharge could have occurred in the subsurface via the network of normal faults that have locally juxtaposed basement and aquifer on the southern flank of the Highlands (thereby bypassing the intervening Anhydrite Group seal). Either way, the infiltration of the modified surface water must have occurred early in the Neogene history of regional uplift, because the parent water of calcite + kaolinite in the dissolution cavities has significantly higher  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{18}\text{O}$  signatures than Holocene groundwater (Fig. 2a,c).

#### 4. Conclusions

The above evidence demonstrates that dissolution of anhydrite nodules and associated precipitation of quartz and later calcite + kaolinite in the Upper Muschelkalk aquifer are all due to recharge by meteoric runoff from the Black Forest crystalline basement, which outcrops immediately to the north of the Swiss Molasse Basin. The depth to which this water infiltrated the aquifer (e.g. in the Mid-Miocene) would have been limited by regional hydraulic gradients. Consequently, the high porosity created by anhydrite dissolution is likely to be only a local phenomenon, spatially restricted to the northern margin of the Basin. This result argues against the occurrence of cavernous porosity and its associated high matrix permeability in the south of the SMB, where temperatures and depths are more conducive to geothermal energy and gas-storage applications. Exploration in the deeper realms of the Basin should therefore target other types of porosity and permeability, e.g. sucrosic dolomite facies and fracture networks.

#### References

1. Chevalier G, Diamond LW, Leu W. Potential for deep geological sequestration of  $\text{CO}_2$  in Switzerland: a first appraisal. *Swiss Journal of Geosciences* 2010;**103**(3):427-455.
2. Nagra. *Projekt Opalinuston: Synthese der geowissenschaftlichen Untersuchungsergebnisse*. Nagra Technischer Bericht NTB 02-03. Wettingen: Nagra; 2002.
3. Nagra. *Sondierbohrung Benken – Untersuchungsbericht*. Nagra Technischer Bericht NTB 00-01. Wettingen: Nagra; 2001.
4. *A combined petrographic, sedimentological, geochemical and petrophysical study*. Bern: Institute of Geological Sciences; 2013.
5. Thury M, Gautschi A, Mazurek M, Müller WH, Naef H, Pearson FJ, Vomvoris S, Wilson W. *Geology and Hydrogeology of the Crystalline Basement of Northern Switzerland*. Nagra Technischer Bericht NTB 93-01. Wettingen: Nagra; 1994.
6. O'Neil JR, Clayton RN, Mayeda TK. Oxygen isotope fractionation in divalent metal carbonates. *J Chem Phys* 1969;**51**:5547-5558.
7. Zheng YF. Calculation of oxygen isotope fractionation in anhydrous silicate minerals. *Geochim Cosmochim Acta* 1993;**57**:1079-1091.
8. Sheppard SMF, Gilg HA. Stable isotope geochemistry of clay minerals. *Clay Minerals* 1996;**31**:1-24.
9. Matter A, Peters T, Ramseyer K.  $^{87}\text{Sr}/^{86}\text{Sr}$ -Verhältnisse und Sr-Gehalte von Tiefengrundwässern, Mineralien sowie Gesteinen aus dem Kristallin und der Trias der Nordschweiz. *Eclogae Geologicae Helveticae* 1987;**80**:579-592.